

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 10-227931

(43)Date of publication of application : 25.08.1998

(51)Int.Cl. G02B 6/12
C08L 27/12
C08L 29/10
G02B 1/04

(21)Application number : 09-042874

(71)Applicant : NIPPON TELEGR & TELEPH CORP
<NTT>

(22)Date of filing : 13.02.1997

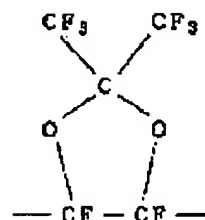
(72)Inventor : MARUNO TORU
KOBAYASHI JUNYA
KOSHIYOSU NOBUTAKE
MATSUURA TORU
SASAKI SHIGEKUNI

(54) WAVEGUIDE TYPE OPTICAL DEVICE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a polymer waveguide optical device excellent in heat resistance, water and moisture resistance and light-transmitting property and improved in cost performance and versatility.

SOLUTION: In this waveguide optical device including a directional coupler, the core and/or the clad of the directional coupler essentially consists of the perfluoro org. polymer material described below as the main structural element. This polymer material is an amorphous org. polymer material which has a cyclic structure comprising carbon-carbon single bonds and carbon-oxygen single bonds in the molecular chain expressed by formula and has only carbon-fluorine bonds as chemical bonds of carbon and univalent elements. The waveguide optical device may contain a Mach-Zehnder interferometer fabricated by the combination of two or more directional couplers. Moreover, the device may have a thermo-optic phase shifter consisting of a resistor thin film for electric heating.



LEGAL STATUS

[Date of request for examination] 16.01.2001

[Date of sending the examiner's decision of rejection] 28.10.2002

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision
of rejection]

[Date of requesting appeal against examiner's
decision of rejection]

[Date of extinction of right]

Copyright (C); 1998,2003 Japan Patent Office

* NOTICES *

JPO and NCIPJ are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.*** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] The waveguide type light device characterized by forming the perfluoro-organic polymeric materials which are the amorphous organic polymeric materials which have the cyclic structure to which the core of this directional coupler and either of the clads, or both ingredients consist of carbon-carbon single association and carbon-oxygen single association into a chain in the waveguide type light device containing a directional coupler, and include only carbon-fluorine association as a chemical bond of carbon and a monad as a main component.

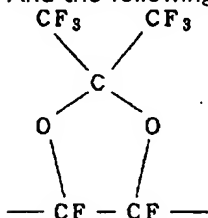
[Claim 2] The waveguide type light device according to claim 1 characterized by including the Mach-Zehnder interferometer produced combining two or more directional couplers.

[Claim 3] The waveguide type light device according to claim 1 characterized by having the heat optical phase shifter which consists of a resistor thin film for performing energization heating.

[Claim 4] these perfluoro-organic polymeric materials -- following structure-expression (** 1): -

- [Formula 1]
-CF₂-CF₂-

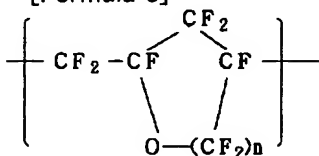
And the following structure expression (** 2): [Formula 2]



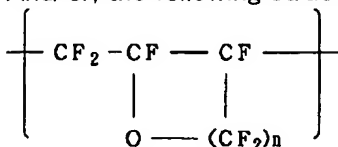
since -- a waveguide type light device given in any 1 term of claims 1-3 characterized by being the becoming copolymer.

[Claim 5] these perfluoro-organic polymeric materials -- following structure-expression (** 3): -

- [Formula 3]



And/or, the following structure expression (** 4): [Formula 4]



(-- however, a waveguide type light device given in any 1 term of claims 1-3 characterized by each n having the repeat unit expressed with 1 or 2).

[Translation done.]

* NOTICES *

JPO and NCIPJ are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.

2. **** shows the word which can not be translated.

3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the waveguide type light device formed using the perfluoro-organic polymeric materials which are the amorphous organic polymeric materials which have the cyclic structure which consists of carbon-carbon single association and carbon-oxygen single association, and include only carbon-fluorine association as a chemical bond of carbon and a monad into the chain.

[0002]

[Description of the Prior Art] Researches and developments of various optical components are furthered towards the advancement of an optical transmission system, and economization. Especially, optical waveguide attracts attention as a basic technique to high density light wiring and waveguide type light device implementation. Generally, from an optical waveguide ingredient, the ease of waveguide production, the controllability of a refractive index, thermal resistance, waterproof moisture resistance, etc. are required. As current and an optical waveguide ingredient, the quartz is used best, and, as for the optical waveguide made from a quartz, the wavelength of 1.3 micrometers shows the low optical loss of 0.1 or less dB/cm. However, complexity and large area-ization have which difficult trouble and a manufacture process cannot obtain easily the waveguide type light device which is excellent in economical efficiency and versatility. On the other hand, since macromolecule optical waveguide can use the membrane formation process by the spin coat method, as compared with quartz system optical waveguide, it is simple for a production process and large-area-izing is also easy for it. Furthermore, especially the application of polymeric materials to the waveguide type light device which had the heat optical (TO) effectiveness (temperature dependence of a refractive index) big 10 or more times compared with the quartz in many cases, and used the TO effectiveness is promising. The temperature dependence of a refractive index compares polymethylmethacrylate (PMMA) with less than [of $-1.0 \times 10^{-4}/\text{degree C}$ and a quartz $1 \times 10^{-5}/\text{degree C}$]. For example, since it is large 10 or more times, When PMMA optical waveguide is applied to a Mach TSUENDA mold TO switch (HIDA (Hida) others by which it is known that switching power will be greatly reduced by about 1/100 compared with quartz system optical waveguide, IEEE Photonics Technology Letters (IEEE Photonics Technology Letters), the 5th volume, the 782page(1993)). However, since heat deflection temperature of PMMA is as low as about 100 degrees C, a switching characteristic deteriorates by the repeat of [Fumio Ide work, "optoelectronics and a macromolecule", the 28th page and KYORITSU SHUPPAN (1995)], and heating and cooling at the time of actuation. For this reason, it cannot be said that PMMA is suitable for the waveguide type light device formation using the TO effectiveness. Moreover, water absorption of PMMA is as large as about 2%, and a refractive index changes with environmental humidity a lot. For example, when the directional coupler which is the most fundamental element of optical components is formed using PMMA, the branching ratio of outgoing radiation light will change with installation environments a lot. Furthermore, since the absorption of 1.55-micrometer band of PMMA is large, [Yoshimura et al., a "flat-surface mold polymer light wave circuit", the collection of the Institute of Electronics, Information and Communication Engineers spring

convention drafts, SC-8-3, 5-319 (1994)] and the components for optical communication in this wavelength range also have the fault that it cannot be used. Thus, as an ingredient of a waveguide type light device, the polymeric materials which were excellent in thermal resistance, waterproof moisture resistance, and the light transmission nature in long wavelength are needed.

[0003] As heat-resistant outstanding polymeric materials, polyimide is known well and used for the interlayer insulation film of semi-conductor components, the flexible wiring substrate, etc. However, usual polyimide is inferior to the light transmission nature of the near-infrared region (1.3 micrometers, 1.55 micrometers) where hygroscopicity is not only large but an optical-communication wavelength range. Then, the fluorination polyimide which introduced the fluorine substituent is proposed as an ingredient in which optical application is possible, holding the thermal resistance of polyimide. It is already shown clearly that fluorination polyimide is transparent in a near-infrared region (JP,3-72528A) and that it excels in waterproof moisture resistance. Furthermore, the method (JP,4-235505A, 4-235506) of forming the fluorination polyimide optical waveguide using this refractive-index control is also easily shown that a refractive index is changeable (JP,4-8734A) by controlling a copolymerization ratio, using this fluorination polyimide as a copolymer. Although moisture absorption is small compared with 0.2 - 0.7%, PMMA, etc. also about fluorination polyimide, there is a fault that effect of moisture to a directional coupler property or the property of a Mach-Zehnder interferometer cannot be disregarded. When TO switch is especially produced with these ingredients, since the adsorption and desorption of moisture happen by carrying out energization heating, a refractive index may change a lot and may exceed the refractive-index change by the TO effectiveness. For this reason, there was also a fault of being hard to obtain the object which an operating characteristic changes a lot and is equal to practical use with environmental humidity. There is optical waveguide (JP,4-190202A) using the polymeric materials which are excellent in thermal resistance, waterproof moisture resistance, and the light transmission nature in long wavelength using perfluoro-organic polymeric materials as an example of another waveguide production. 0.1 or less dB/cm is realized as waveguide loss of 1.3-micrometer band of ridge mold waveguide, and it is checked that after one-week immersion does not have property change into 60-degree-C warm water. However, there is no example of application to the waveguide mold device which contains the directional coupler of perfluoro-organic polymeric materials until now. Furthermore, since the thermooptic effect of perfluoro-organic polymeric materials has not inquired, it does not have an example of application using a thermooptic effect, either.

[0004]

[Problem(s) to be Solved by the Invention] The purpose of this invention offers the giant-molecule waveguide type light device which is excellent in thermal resistance, waterproof moisture resistance, and light transmission nature, and is to improve the economical efficiency of a waveguide type light device, and versatility as the result.

[0005]

[Means for Solving the Problem] If this invention is outlined, this invention has the cyclic structure which consists of carbon-carbon single association and carbon-oxygen single association into a chain. And it is invention about the waveguide type light device using the perfluoro-organic polymeric materials which are the amorphous organic polymeric materials which include only carbon-fluorine association as a chemical bond of carbon and a monad. The waveguide type light device of the 1st invention is characterized by either a core and a clad and both containing the directional coupler formed considering perfluoro-organic polymeric materials as a main component. The waveguide type light device of the 2nd invention is characterized by including the Mach-Zehnder interferometer produced combining two or more directional couplers of the 1st invention. The waveguide type light device of the 3rd invention is characterized by having the heat optical phase shifter which the waveguide type light device of the 1st invention becomes from the resistor thin film for performing energization heating. For the waveguide type light device of the 4th invention, the perfluoro-organic polymeric materials in the waveguide type light device of the 1st - the 3rd invention are following structure-expression (** 1): [0006]. [Formula 1]

<http://www4.ipdl.ncipi.go.jp/cgi-bin/tran/web.cgi.ejje>

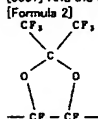
2005/12/21

<http://www4.ipdl.ncipi.go.jp/cgi-bin/tran/web.cgi.ejje>

2005/12/21

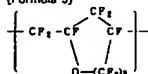
-CF₂-CF₂-

[0007] And the following structure expression (** 2): [0008]



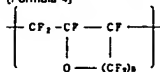
[0009] since -- it is characterized by being the becoming copolymer. Furthermore, for the waveguide type light device of the 5th invention, the perfluoro-organic polymeric materials in the waveguide type light device of the 1st - the 3rd invention are following structure-expression (** 3): [0010].

[Formula 3]



[0011] And/or, the following structure expression (** 4): [0012]

[Formula 4]



[0013] (--- however, each n is characterized by having the repeat unit expressed with 1 or 2).

[0014] As a result of advancing examination from the aforementioned viewpoint, the perfluoro-organic polymeric materials which are the amorphous organic polymeric materials which this invention persons have the cyclic structure which consists of carbon-carbon single association and carbon-oxygen single association into a chain, and include only carbon-fluorine association as a chemical bond of carbon and a monad showed clearly that it has workability required for waveguide type light device production containing a directional coupler. Consequently, it came to complete header this invention for that the produced device is excellent also in thermal resistance and waterproof moisture resistance with low loss in the wavelength of 1.3 micrometers, and a 1.55-micrometer near-infrared region, and the heat optical constant temperature dependence of a refractive index is indicated to be being equivalent to other polymeric materials (more than $10^{-4}/\text{degree C}$), and it being larger than a quartz enough.

[0015]

[Embodiment of the Invention] Hereafter, this invention is explained concretely. A clad and core materials applicable to this invention are explained. In order to demonstrate the engine performance stable [a waveguide type light device's], as mentioned above, thing ** with the environmental humidity dependency of a refractive index small [that 1 waveguide ingredient is transparent a near-infrared region especially the wavelength of 1.3 micrometers, and near 1.55 micrometer, two clads, and core materials] at low moisture absorption and low water absorption is desired. Furthermore, it becomes important [a clad the heat optical constant of core materials, and thermal resistance] in the case of the waveguide type light device using a thermooptic effect.

[0016] The absorption spectrum of the copolymer (a copolymerization ratio, 35:65 mole ratios) of the compound expressed with a formula (** 1) and the compound expressed with a formula (** 2) is shown in drawing 1 R> 1 as compared with PMMA. drawing 1 --- setting --- a continuous line

--- the copolymer concerned and a broken line --- each of PMMA --- an absorption spectrum is shown.

[0017] As shown in drawing 1, since perfluoro-organic polymeric materials do not have harmonic-overtone absorption of vibration of C-H coupling the wavelength of 1.1 micrometers which was not able to be removed, 1.4 micrometers, and near 1.65 micrometer, they have high transparency throughout 0.6-1.7 micrometers with an organic compound including the conventional C-H coupling. Moreover, the above-mentioned copolymer, the compound which has the repeat structure of n=1 by the formula (** 3), and the compound which has the repeat structure of n=2 by the formula (** 4) are ASTM about the film sample. Perfluoro-organic polymeric materials have 1/20 or less small water absorption also to 1/100 or less [of usual PMMA], and fluorination polyimide so that it may understand also from the water absorption measured by the approach of D570 being 0.01% or less. For this reason, the directional coupler produced using the perfluoro-organic macromolecule is not based on environmental humidity, but shows a fixed property, and can produce the waveguide type light device excellent in the environmental humidity dependency. In the waveguide type light device using the perfluoro-organic giant molecule of this invention to harmonic-overtone absorption of vibration of O-H association with a wavelength of 1.4 micrometers having increased according to moisture absorption in the conventional polymeric materials, and the increment in optical loss (1.3 micrometers and 1.55 micrometers) having been observed especially, loss fluctuation was a small value also in high humidity conditions. Furthermore, switching power became about 1/100 compared with quartz system optical waveguide, and the Mach TSUENDA mold thermooptic effect switch produced by perfluoro-organic polymeric materials had the big thermooptic effect comparable as the case of PMMA. Moreover, the humidity dependency of a switching characteristic was not observed, either but the stable property has been realized.

[0018] As perfluoro-organic polymeric materials used for this invention, it does not have C-H coupling in intramolecular, but if it is amorphous plastics which includes only carbon-fluorine association as a chemical bond of carbon and a monad, anything can be used. The plastics which has cyclic ether structure, i.e., the cyclic structure which consists of carbon-carbon single association and carbon-oxygen single association, can use it suitably into the principal chain structure of a macromolecule from a viewpoint which suppresses dispersion of the light accompanying an orientation birefringence by abolishing the symmetric property in the molecular structure of plastics, and raising amorphism nature especially.

[0019] Hereafter, the optical waveguide device of this invention is explained more to a detail. A directional coupler and the general making process of a Mach-Zehnder interferometer are shown in drawing 2 among the optical waveguide devices of this invention. First, the lower cladding layer 2 is formed on a substrate 1. Next, the core layer 3 with a bigger refractive index than the lower cladding layer 2 is formed in up to the lower cladding layer 2. Next, the mask pattern 4 of a directional coupler or a Mach-Zehnder interferometer is formed in up to a core layer 3 with a FOTORISO graphic method. The core pattern 5 of a dead directional coupler is formed for etching to the core layer 3 in which the mask pattern 4 was formed using the RIE method. After removing a mask, the up cladding layer 6 is formed on the core pattern 5 of a directional coupler. By such approach, the directional coupler (drawing 3) by perfluoro-organic macromolecule optical waveguide and a Mach-Zehnder interferometer (drawing 4) are formed. That is, drawing 3 and drawing 4 are each mimetic diagram.

[0020] A directional coupler is one of the things the most important in the element which constitutes a waveguide type light device, and fundamental. It is used as optical components which branch outgoing radiation light by the ratio of arbitration, and the branching ratio can be controlled by the simple substance by changing interaction length. Moreover, a Mach-Zehnder interferometer is a basic optical circuit which constitutes a waveguide type light device, and can be used as various optical components with combination with a phase shifter. In this invention, even if it carried out long duration use by the high temperature service or the high-humidity/temperature condition using the thermal resistance of the perfluoro-organic polymeric materials used as a waveguide ingredient, waterproof moisture resistance, and an optical loss property being excellent, the small directional coupler and small Mach-Zehnder interferometer of

<http://www4.ipdl.ncipi.go.jp/cgi-bin/tran/web.cgi.ejje>

2005/12/21

<http://www4.ipdl.ncipi.go.jp/cgi-bin/tran/web.cgi.ejje>

2005/12/21

property change could be produced easily, and the resistance to environment of the waveguide type light device which has a directional coupler and a Mach-Zehnder interferometer, economical efficiency, and versatility improved sharply.

[0021] Drawing 3 is the Mach-Zehnder interferometer formed using perfluoro-organic macromolecule optical waveguide, and drawing showing the making process of TO switch which consists of an electrode for heating by the resistor thin film. A metal membrane 7 is formed on the up cladding layer 6 of the Mach-Zehnder interferometer produced by the same approach as drawing 2. Next, after forming the mask pattern 8 of the electrode for heating (heat optical phase shifter) in up to this metal membrane 7 with a FOTORISO graphic method, etching of a metal membrane 7 is performed and the electrode 9 for heating is formed. By such approach, the Mach TSUENDA mold TO switch (drawing 8, mimetic diagram) by perfluoro-organic giant-molecule optical waveguide is formed. In this invention, since the perfluoro-organic giant molecule which excelled [ingredient / optical waveguide] in thermal resistance and waterproof moisture resistance was used, it excels in a resistance to environment and long term stability, and the perfluoro-organic giant-molecule TO switch switched at low power and a high speed rather than a quartz system TO switch could form easily, moreover, it also turned out that the operating characteristic of about 1 law is shown under large humidity conditions also in the condition of not taking measures, such as the closure which prevents invasion of moisture or moisture, compared with TO switch produced by other polymeric materials. Consequently, the resistance to environment of a giant-molecule TO switch, economical efficiency, and versatility were able to be raised sharply. In addition, in this invention, although the substrate ingredient of arbitration can be used, as for a switching rate, the direction which used substrate ingredients, such as aluminum with the big heat conductivity, aluminum alloy, stainless steel, and copper, becomes easy. Moreover, as an ingredient for resistor thin film formation, Ti, Cr, aluminum, gold, silver, copper, platinum, the tin oxide, indium oxide, indium tin oxide, and such mixture can be used. Moreover, you may be the cascade screen of these thin films.

[0022] In addition, in the making process of the waveguide type light device shown above, when carrying out the spin coat of the core materials on the charge of a clad plate, and when carrying out the spin coat of the charge of a clad plate on core materials, INTAMIKISHINGU mixed with the ingredient which the ingredient applied previously dissolves and is applied later may occur. It cannot be overemphasized that the INTAMIKISHINGU prevention layer of a thin film may be prepared in this invention using an ingredient without a core, a clad, and a common solvent, the ingredient of this prevention layer — which of in inorganic material and an organic material — — as an inorganic material — SiO_2 MgF_2 and CaF_2 etc. — moreover, as an organic material, polyimide, a silicon macromolecule, etc. can be used other than a perfluoro-organic macromolecule. The production approach has the spin-on glass method besides various vacuum deposition methods, such as resistance heating, electron beam heating, and sputtering, and an available spin coat method.

[0023]

[Example] Hereafter, although this invention is explained still more concretely using a drawing, this invention is not limited to these examples. In addition, at this example, although Ti and gold are used for the substrate at a ceramic, silicon, and a metal membrane, it cannot be overemphasized that other ingredients may be used.

[0024] they are the tetrafluoroethylene which is the structure of example 1 formula (≡ 1), and the structure of a formula (≡ 2) — bis — among copolymers with -2, 2-trifluoromethyl-4, 5-difluoro-1, and 3-JIOKI SOL (PPD), the copolymerization ratio of PPD dissolved the 83-mol % of macromolecule in the organic solvent (Fluorinert FC-75, 3 M company make) of a fluorine system so that concentration might become 2%. The spin coat of the solution was carried out on the ceramic substrate, and under nitrogen-gas-atmosphere mind, it heated at 40 degrees C for 1 hour, and heated at 180 degrees C by 100 degrees C for 1 hour, the solvent was removed completely, and 15 micrometers of thickness and a refractive index with a wavelength of 0.59 micrometers produced the lower cladding layer 2 of 1.29. Next, the copolymerization ratio of PPD dissolves 40-mol % of a macromolecule in the organic solvent (Fluorinert FC-75, 3 M company make) of a fluorine system so that concentration may become 10%, and it carries out

<http://www4.ipdl.ncipi.go.jp/cgi-bin/tran/web.cgi.ejie>

2005/12/21

waveguide with a core width of face [of 7 micrometers] and a core height of 7 micrometers was obtained by changing the mask pattern 4 of example 3 example 1 into the Mach-Zehnder interferometer of the structure which connected two 3dB couplers, and performing the same actuation as an example 1. When light with a wavelength of 1.3 micrometers was inputted into this Mach-Zehnder interferometer from the arm 1, the optical output was observed only with the arm 4. The insertion loss at this time showed 2.5dB and a small value by joint loss lump. The produced Mach-Zehnder interferometer has the property equivalent to the first stage, even after being immersed after 100-degree-C heat treatment and underwater, and into a high-humidity/temperature (85-degree-C, 85%RH) ambient atmosphere and an acetone, and it was excellent in a resistance to environment and long term stability. Moreover, environmental humidity showed the almost equivalent property in the range of RH 13 to 90%, and the humidity dependency of the branching ratio which was a problem in the conventional macromolecule waveguide of operation was also canceled. Furthermore, it was possible by using 3dB coupler on the wavelength of 1.2 micrometers - 1.65 micrometers to have obtained the same result as the case of 1.3 micrometers in a full wave length region. Consequently, the resistance to environment of the waveguide type light device which has a Mach-Zehnder interferometer, economical efficiency, and versatility improved sharply by using the perfluoro-giant molecule of the copolymer of a formula (≡ 1) and a formula (≡ 2).

[0027] The Mach-Zehnder interferometer of the structure of drawing 4 formed by flush type waveguide with a core width of face [of 7 micrometers] and a core height of 7 micrometers was obtained by changing the mask pattern 4 of example 4 example 2 into the Mach-Zehnder interferometer of the structure which connected two 3dB couplers, and performing the same actuation as an example 2. When light with a wavelength of 1.3 micrometers was inputted into this Mach-Zehnder interferometer from the arm 1, the optical output was observed only with the arm 4. The insertion loss at this time showed 2.6dB and a small value by joint loss lump. The produced Mach-Zehnder interferometer has the property equivalent to the first stage, even after being immersed after 100-degree-C heat treatment and underwater, and into a high-humidity/temperature (85-degree-C, 85%RH) ambient atmosphere and an acetone, and it was excellent in a resistance to environment and long term stability. Moreover, environmental humidity showed the almost equivalent property in the range of RH 13 to 90%, and the humidity dependency of the branching ratio which was a problem in the conventional macromolecule waveguide of operation was also canceled. Furthermore, it was possible by using 3dB coupler on the wavelength of 1.2 micrometers - 1.65 micrometers to have obtained the same result as the case of 1.3 micrometers in a full wave length region. Consequently, the resistance to environment of the waveguide type light device which has a Mach-Zehnder interferometer, economical efficiency, and versatility improved sharply by using the poly perfluoro-allyl vinyl ether which has the repeat structure of $n=1$ by the formula (≡ 3).

[0028] The Ti metal membrane 7 used as the electrode for heating (heat optical phase shifter) was formed by sputter vacuum evaporation on the up cladding layer 6 of the Mach-Zehnder interferometer produced in the example 5 example 3. After carrying out the spin coat of the photoresist to this Ti metal membrane 7, the resist was made to imprint the mask pattern 8 of an electrode with a FOTORISO graphic method. The photoresist was used as the mask. Ti was etched into the last, and the electrode 9 was formed in it. As a result of performing property measurement of the Mach TSUENDA mold TO switch (drawing 6) by the perfluoro-organic giant-molecule optical waveguide formed by such approach, the switching time was 4mS(a), switching power was 8mW, and the extinction ratio of 2.5dB and switching of the insertion loss of the transparency port at this time was 25dB in the connection loss lump. It turned out that the perfluoro-organic giant-molecule TO switch which switching power is 1/50 or less [made from a quartz] and was produced according to the effectiveness of the big heat optical constant which the perfluoro-giant molecule of the copolymer of a formula (≡ 1) and a formula (≡ 2) has operates as low power and a high-speed optical switch. Moreover, produced TO switch has the property equivalent to the first stage, even after being immersed after 100-degree-C heat treatment and underwater, and into a high-humidity/temperature (85-degree-C, 85%RH) ambient atmosphere and an acetone, and it was excellent in a resistance to environment and long term

<http://www4.ipdl.ncipi.go.jp/cgi-bin/tran/web.cgi.ejie>

2005/12/21

the spin coat of the solution on a ceramic substrate. Under nitrogen-gas-atmosphere mind, it heated at 40 degrees C for 1 hour, and heated at 180 degrees C by 100 degrees C for 1 hour for 1 hour, the solvent was removed completely, and 7 micrometers of thickness and a refractive index with a wavelength of 0.59 micrometers produced the core layer 3 of 1.32. Titanium was vapor-deposited with the electron beam heating process as a mask for etching all over this sample. Subsequently, spreading of a positive resist, prebaking, exposure, development, and postbake were performed, patterning of the titanium was carried out by wet etching, and the mask pattern 4 of a directional coupler was produced. Furthermore, this titanium — a mask — carrying out — bis — patterning of the film of a copolymer with tetrafluoroethylene was carried out to -2, 2-trifluoromethyl-4, 5-difluoro-1, and 3-JIOKI SOL (PPD) by dry etching, and the core pattern 5 was produced. Wet etching removed the remaining titanium and the up clad 6 with a thickness of 5 micrometers was produced by the approach same with finally having produced the lower clad. By such approach, the directional coupler of the structure of drawing 3 formed by flush type waveguide with a core width of face [of 7 micrometers] and a core height of 7 micrometers was obtained. The refractive-index difference delta between a core and a clad was about 0.25% on the wavelength of 1.3 micrometers. This directional coupler showed 2dB of insertion losses and 0.2dB of superfluous loss of 3dB coupler whose TE polarization and TM polarization include 97% or more of binding fractions, and connection loss, and the outstanding optical property by choosing interaction length suitably at the time of the wavelength of 1.3 micrometers. Furthermore, in the full wave length region with a wavelength of 1.2 micrometers - 1.65 micrometers, the directional coupler of 2.3dB of insertion losses and 0.3dB or less of superfluous loss of a 3dB coupler with which TE polarization and TM polarization include 95% or more of binding fractions and connection loss was obtained. The produced directional coupler has the property equivalent to the first stage, even after being immersed after 100-degree-C heat treatment and underwater, and into a high-humidity/temperature (85-degree-C, 85%RH) ambient atmosphere and an acetone, and it was excellent in a resistance to environment and long term stability. Consequently, the resistance to environment of the waveguide type light device which has a directional coupler, economical efficiency, and versatility improved sharply by using the perfluoro-giant molecule of the copolymer of a formula (≡ 1) and a formula (≡ 2).

[0025] Instead of the perfluoro-giant molecule (the copolymer of screw -2, 2-trifluoromethyl-4, 5-difluoro-1, and 3-JIOKI SOL (PPD) and tetrafluoroethylene) used as a core layer 3 in example 2 example 1 The poly perfluoro-allyl vinyl ether (the refractive index of a thin film with a wavelength of 0.59 micrometers is 1.34) which has the repeat structure of $n=1$ by the formula (≡ 3) As a spin coat solvent for core layer production, instead of the organic solvent (Fluorinert FC-75, 3 M company make) of a fluorine system moreover, a perfluoro-organic solvent (CT-solv 180, Asahi Glass Co., Ltd. make) The directional coupler of the structure of drawing 3 formed like the example 1 instead of the ceramic plate as a substrate using Si wafer by flush type waveguide with a core width of face [of 7 micrometers] and a core height of 7 micrometers was obtained. The refractive-index difference delta between a core and a clad was about 0.35% on the wavelength of 1.3 micrometers. This directional coupler showed 2dB of insertion losses and 0.2dB of superfluous loss of 3dB coupler whose TE polarization and TM polarization include 97% or more of binding fractions, and connection loss, and the outstanding optical property at the time of the wavelength of 1.3 micrometers. Furthermore, in the full wave length region with a wavelength of 1.2 micrometers - 1.65 micrometers, the directional coupler of 2.3dB or less of insertion losses and 0.3dB or less of superfluous loss of a 3dB coupler with which TE polarization and TM polarization include 95% or more of binding fractions and connection loss was obtained. The produced directional coupler has the property equivalent to the first stage, even after being immersed after 100-degree-C heat treatment and underwater, and into a high-humidity/temperature (85-degree-C, 85%RH) ambient atmosphere and an acetone, and it was excellent in a resistance to environment and long term stability. Consequently, the resistance to environment of the waveguide type light device which has a directional coupler, economical efficiency, and versatility improved sharply by using the poly perfluoro-allyl vinyl ether which has the repeat structure of $n=1$ by the formula (≡ 3).

[0026] The Mach-Zehnder interferometer of the structure of drawing 4 formed by flush type

<http://www4.ipdl.ncipi.go.jp/cgi-bin/tran/web.cgi.ejie>

2005/12/21

stability. Furthermore, environmental humidity showed the almost equivalent property in the range of RH 13 to 90%, and the humidity dependency of the extinction ratio of switching which was a problem in the conventional giant-molecule waveguide of operation was also canceled. Consequently, the resistance to environment of a giant-molecule TO switch, economical efficiency, and versatility were able to be sharply raised by using the perfluoro-giant molecule of the copolymer of a formula (≡ 1) and a formula (≡ 2).

[0029] The two-layer metal membrane 7 of Ti and gold used as the electrode for heating (heat optical phase shifter) was formed by sputter vacuum evaporation on the up cladding layer 6 of the Mach-Zehnder interferometer produced in the example 8 example 4. After carrying out the spin coat of the photoresist to this metal membrane 7, the resist was made to imprint the mask pattern 8 of an electrode with a FOTORISO graphic method. The photoresist was used as the mask. Ti was etched into the last, and the electrode 9 was formed in it. As a result of performing property measurement of the Mach TSUENDA mold TO switch (drawing 8) by the poly perfluoro-allyl-vinyl-ether optical waveguide formed by such approach, the switching time was 5mS(a), switching power was 7mW, and the extinction ratio of 2.6dB and switching of the insertion loss of the transparency port at this time was 25dB in the connection loss lump. It turned out that the perfluoro-organic giant-molecule TO switch which switching power is 1/50 or less [made from a quartz], and was produced by the formula (≡ 3) according to the effectiveness of the big heat optical constant which poly perfluoro-allyl vinyl ether with the repeat structure of $n=1$ has operates as low power and a high-speed optical switch. Moreover, produced TO switch has the property equivalent to the first stage, even after being immersed after 100-degree-C heat treatment and underwater, and into a high-humidity/temperature (85-degree-C, 85%RH) ambient atmosphere and an acetone, and it was excellent in a resistance to environment and long term stability. Furthermore, environmental humidity showed the almost equivalent property in the range of RH 13 to 90%, and the humidity dependency of the extinction ratio of switching which was a problem in the conventional giant-molecule waveguide of operation was also canceled. Consequently, the resistance to environment of a giant-molecule TO switch, economical efficiency, and versatility were able to be sharply raised by using the poly perfluoro-allyl vinyl ether which has the repeat structure of $n=1$ by the formula (≡ 3).

[0030] Instead of the poly perfluoro-allyl vinyl ether which was used in the example 7 example 8 which has the repeat structure of $n=1$ by the formula (≡ 3) The poly perfluoro-ethyl vinyl ether which has the repeat structure of $n=2$ by the formula (≡ 3). The poly perfluoro-allyl vinyl ether which has the repeat structure of $n=1$ by the formula (≡ 4), and the same actuation as an example 6 was performed using the poly perfluoro-allyl vinyl ether which has the repeat structure of $n=2$ by the formula (≡ 4), and the Mach TSUENDA mold TO switch by poly perfluoro-allyl-vinyl-ether optical waveguide was produced. As a result of performing the property measurement, the value with the insertion loss of the switching time, switching power, and a transparency port and the extinction ratio of switching almost equivalent in $\approx 10\%$ of range of the switch produced in the example 6 was shown. Moreover, even after being immersed after 100-degree-C heat treatment and underwater, and into a high-humidity/temperature (85-degree-C, 85%RH) ambient atmosphere and an acetone, it has the property equivalent to the first stage, and it excelled in a resistance to environment and long term stability. Furthermore, environmental humidity showed the almost equivalent property in the range of RH 13 to 90%, and the humidity dependency of the extinction ratio of switching which was a problem in the conventional giant-molecule waveguide of operation was also canceled. Consequently, the resistance to environment of a giant-molecule TO switch, economical efficiency, and versatility were able to be sharply raised also by using the poly perfluoro-allyl vinyl ether which has the repeat structure of $n=2$ by the formula (≡ 3), and the poly perfluoro-ethyl vinyl ether which has the repeat structure of $n=1$ by the formula (≡ 4), and the poly perfluoro-allyl vinyl ether which has the repeat structure of $n=2$ by the formula (≡ 4).

[0031] Partial fluorination PMMA was used as PMMA and a charge of a clad plate as example of comparison 1 core materials, and the Mach-Zehnder interferometer was produced by the same approach as an example 3. When light with a wavelength of 1.3 micrometers was inputted into this Mach-Zehnder interferometer from the arm 1, the optical output was observed only with the

<http://www4.ipdl.ncipi.go.jp/cgi-bin/tran/web.cgi.ejie>

2005/12/21

arm 4 at the time of 50% of environmental humidity. The insertion loss at this time showed 2.3dB and a small value by joint loss lump. However, 1.1 and 1.4 or 1.6-micrometer band with the harmonic-overtone absorption peak of CH association showed the big insertion loss 10dB or more. It turned out that an insertion loss increases the produced Mach-Zehnder interferometer to 5dB or more after being immersed after 100-degree-C heat treatment and underwater, and into a high-humidity/temperature (85-degree-C, 85%RH) ambient atmosphere and an acetone, and a resistance to environment and long term stability are inferior. Moreover, the output of an arm 4 decreased [environmental humidity] gradually in the range of RH 13 to 90%, and the output of an arm 3 increased. Consequently, in the Mach-Zehnder interferometer which uses PMMA as core materials, a resistance to environment, economical efficiency, and versatility are inferior.

[0032] Partial fluorination PMMA was used as PMMA and a charge of a clad plate as example of comparison 2 core materials, and the Mach-Zehnder-interferometer mold TO switch was produced by the same approach as an example 5. As a result of performing property measurement of this Mach TSUENDA mold TO switch (drawing 6), the switching time was 5mS (s), switching power was 8mW, and the extinction ratio of 2.5dB and switching of the insertion loss of the transparency port at this time was 25dB in the connection loss lump. When the property was measured after immersing produced TO switch after 100-degree-C heat treatment and underwater, and into a high-humidity/temperature (85-degree-C, 85%RH) ambient atmosphere and an acetone, the insertion loss increased to 5dB or more, and a resistance to environment and long term stability were inferior. Moreover, when environmental humidity is changed in the range of RH 13 to 90%, the extinction ratio of switching by the same operating condition is the worst, falls to 5dB, and serves as an operating characteristic inadequate as an optical switch. Consequently, with the Mach-Zehnder-interferometer mold TO switch which uses PMMA as core materials, a resistance to environment, economical efficiency, and versatility are inferior.

[0033]

[Effect of the Invention] According to this invention, the macromolecule waveguide type light device which is excellent in thermal resistance, waterproof moisture resistance, and an optical loss property can be offered according to the description heat-resistant [of the perfluoro-organic macromolecule used as a waveguide ingredient], waterproof damp-proof one, and Takamitsu penetrable. Moreover, the waveguide type light device which is excellent in economical efficiency and versatility as the result can be manufactured now.

[Translation done.]

• NOTICES •

JPO, and NCIPJ are not responsible for any damages caused by the use of this translation.

1.This document has been translated by computer. So the translation may not reflect the original precisely.

2.*** shows the word which can not be translated.

3.In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is drawing showing a perfluoro-macromolecule and the absorption spectrum of PMMA.

[Drawing 2] It is drawing showing the making process of a directional coupler and a Mach-Zehnder interferometer.

[Drawing 3] It is the mimetic diagram of a directional coupler.

[Drawing 4] It is the mimetic diagram of a Mach-Zehnder interferometer.

[Drawing 5] It is drawing showing the making process of TO switch by fluorination polyimide.

[Drawing 6] It is the mimetic diagram of a fluorination polyimide TO switch.

[Description of Notations]

1: A substrate, 2:lower cladding layer, 3:core layer, 4:mask pattern, five :core patterns, a 6:up cladding layer, 7:metal membrane, the mask pattern of 8:electrode, 9 : electrode

[Translation done.]

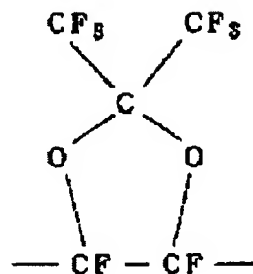
WAVEGUIDE TYPE OPTICAL DEVICE

Patent number: JP10227931
Publication date: 1998-08-25
Inventor: MARUNO TORU; KOBAYASHI JUNYA; KOSHIYOUNBU NOBUTAKE; MATSUURA TORU; SASAKI SHIGEKUNI
Applicant: NIPPON TELEGRAPH & TELEPHONE
Classification:
- international: (IPC1-7): G02B6/12; C08L27/12; C08L29/10; G02B1/04
- european:
Application number: JP19970042874 19970213
Priority number(s): JP19970042874 19970213

Report a data error here

Abstract of JP10227931

PROBLEM TO BE SOLVED: To provide a polymer waveguide optical device excellent in heat resistance, water and moisture resistance and light-transmitting property and improved in cost performance and versatility. **SOLUTION:** In this waveguide optical device including a directional coupler, the core and/or the clad of the directional coupler essentially consists of the perfluoro org. polymer material described below as the main structural element. This polymer material is an amorphous org. polymer material which has a cyclic structure comprising carbon-carbon single bonds and carbon-oxygen single bonds in the molecular chain expressed by formula and has only carbon-fluorine bonds as chemical bonds of carbon and univalent elements. The waveguide optical device may contain a Mach-Zehnder interferometer fabricated by the combination of two or more directional couplers. Moreover, the device may have a thermo-optic phase shifter consisting of a resistor thin film for electric heating.



Data supplied from the **esp@cenet** database - Worldwide

(19) 日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11) 特許出願公開番号

特開平10-227931

(43) 公開日 平成10年(1998) 8月25日

(51) Int.Cl.⁸

識別記号

F I

G 0 2 B 6/12

G 0 2 B 6/12

N

C 0 8 L 27/12

C 0 8 L 27/12

29/10

29/10

G 0 2 B 1/04

G 0 2 B 1/04

審査請求 未請求 請求項の数 5 F D (全 9 頁)

(21) 出願番号 特願平9-42874

(71) 出願人 000004226

日本電信電話株式会社

東京都新宿区西新宿三丁目19番2号

(22) 出願日 平成9年(1997) 2月13日

(72) 発明者 丸野 透

東京都新宿区西新宿三丁目19番2号 日本

電信電話株式会社内

(72) 発明者 小林 潤也

東京都新宿区西新宿三丁目19番2号 日本

電信電話株式会社内

(72) 発明者 小勝負 信雄

東京都新宿区西新宿三丁目19番2号 日本

電信電話株式会社内

(74) 代理人 弁理士 中本 宏 (外2名)

最終頁に続く

(54) 【発明の名称】 導波路型光デバイス

(57) 【要約】

【課題】 耐熱性、耐水耐湿性、光透過性に優れ、かつ経済性、汎用性を改善した高分子導波路型光デバイスを提供する。

【解決手段】 方向性結合器を含む導波路型光デバイスにおいて、該方向性結合器のコア及び／又はクラッドの材料が、分子鎖中に炭素-炭素-重結合と炭素-酸素-重結合からなる環状構造を有し、かつ炭素と一価元素の化学結合として炭素-フッ素結合のみを含む非晶質有機高分子材料であるヘルフルオロ有機高分子材料を主構成要素として形成されている導波路型光デバイス。該デバイスは方向性結合器を2個以上組合せて作製したマッハツェンダー干渉計を含んでいてもよい。また、通電加熱を行うための抵抗体薄膜からなる熱光学位相シフタを有していてもよい。

【特許請求の範囲】

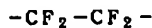
【請求項1】 方向性結合器を含む導波路型光デバイスにおいて、該方向性結合器のコア及びクラッドのいずれか、若しくは両方の材料が、分子鎖中に炭素-炭素-重結合と炭素-酸素-重結合からなる環状構造を有し、かつ炭素と一価元素の化学結合として炭素-フッ素結合のみを含む非晶質有機高分子材料であるペルフルオロ有機高分子材料を主構成要素として形成されていることを特徴とする導波路型光デバイス。

【請求項2】 方向性結合器を2個以上組合せて作製したマッハツェンダー干渉計を含むことを特徴とする請求項1に記載の導波路型光デバイス。

【請求項3】 通電加熱を行うための抵抗体薄膜からなる熱光学位相シフタを有することを特徴とする請求項1に記載の導波路型光デバイス。

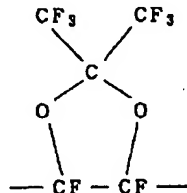
【請求項4】 該ペルフルオロ有機高分子材料が、下記構造式(化1)：

【化1】



及び下記構造式(化2)：

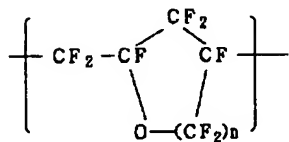
【化2】



からなる共重合体であることを特徴とする請求項1～3のいずれか1項に記載の導波路型光デバイス。

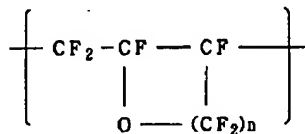
【請求項5】 該ペルフルオロ有機高分子材料が、下記構造式(化3)：

【化3】



及び/又は下記構造式(化4)：

【化4】



(ただし、nはいずれも1又は2)で表される繰り返し単位を有することを特徴とする請求項1～3のいずれか1項に記載の導波路型光デバイス。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、分子鎖中に炭素-

炭素-重結合と炭素-酸素-重結合からなる環状構造を有し、かつ炭素と一価元素の化学結合として炭素-フッ素結合のみを含む非晶質有機高分子材料であるペルフルオロ有機高分子材料を用いて形成した導波路型光デバイスに関する。

【0002】

【従来の技術】光通信システムの高度化、経済化に向けて、様々な光部品の研究開発が進められている。中でも、光導波路は高密度光配線、導波路型光デバイス実現への基本技術として注目されている。一般に、光導波路材料に対しては、導波路作製の容易性、屈折率の制御性、耐熱性、耐水耐湿性等が要求される。現在、光導波路材料としては石英が最もよく利用されており、石英製光導波路は波長1.3μmで0.1dB/cm以下の低光損失を示す。しかしながら、製造プロセスが複雑、大面積化が困難などの問題点を有し、経済性、汎用性に優れた導波路型光デバイスを得にくい。一方、高分子光導波路はスピンコート法による成膜プロセスを利用できるため、石英系光導波路と比較して、作製プロセスが簡単で、大面積化も容易である。更に高分子材料は石英に比べて10倍以上大きな熱光学(TO)効果(屈折率の温度依存性)を持つ場合が多く、TO効果を利用した導波路型光デバイスへの応用が特に有望である。例えば、ポリメチルメタクリレート(PMMA)は屈折率の温度依存性が、 $-1.0 \times 10^{-4}/^{\circ}\text{C}$ と石英の $1 \times 10^{-5}/^{\circ}\text{C}$ 以下に比べて10倍以上大きい。PMMA光導波路をマッハツェンダー型TOスイッチへ応用した場合に、スイッチング電力は石英系光導波路に比べて1/100程度に大きく低減されることが知られている【ヒダ(Hida)ほか、IEEE フォトニクス テクノロジー レターズ (IEEE Photonics Technology Letters)、第5巻、第782頁(1993)】。しかしながら、PMMAは熱変形温度が100℃程度と低いため【井出文雄著、“オプトエレクトロニクスと高分子”、第28頁、共立出版(1995)】、動作時の加熱・冷却の繰り返しによってスイッチング特性が劣化する。このため、PMMAはTO効果を利用した導波路型光デバイス形成に適しているとはいえない。また、PMMAは吸水率が約2%と大きく、屈折率が環境湿度によって大きく変化する。例えば、光部品の最も基本的な要素である方向性結合器をPMMAを用いて形成した場合には、設置環境によって出射光の分岐比は大きく変化してしまう。更には、PMMAは1.55μm帯の吸収が大きい【吉村ら、“平面型ポリマ光波回路”、電子情報通信学会春期大会予稿集、SC-8-3、5-319(1994)】、この波長帯での光通信用部品には使用できないという欠点もある。このように、導波路型光デバイスの材料としては、耐熱性、耐水耐湿性、長波長での光透過性の優れた高分子材料が必要となる。

【0003】耐熱性の優れた高分子材料としてはポリイ

ミドがよく知られており、半導体部品の層間絶縁膜、フレキシブル配線基板などに用いられている。しかしながら、通常のポリイミドは吸湿性が大きいだけでなく、光通信波長帯である近赤外域（1.3 μm 、1.55 μm ）の光透過性に劣る。そこで、ポリイミドの耐熱性を保持しつつ光学応用可能な材料として、フッ素置換基を導入したフッ素化ポリイミドが提案されている。フッ素化ポリイミドは、近赤外域で透明であること（特開平3-72528号）、耐水耐湿性に優れていることが既に明らかにされている。更に、このフッ素化ポリイミドを共重合体として用い共重合比を制御することにより容易に屈折率を変えられること（特開平4-8734号）

と、この屈折率制御を利用したフッ素化ポリイミド光導波路の形成法（特開平4-235505号、同4-235506号）も示されている。フッ素化ポリイミドについても吸湿率は0.2~0.7%とPMMA等比べて小さいものの、方向性結合器特性やマッハツェンダー干渉計の特性に対する水分の影響が無視できないという欠点がある。特に、これらの材料でTOスイッチを作製した場合、通電加熱することにより水分の吸脱着が起こるため屈折率が大きく変化し、TO効果による屈折率変化を上回ってしまうことがある。このため、環境湿度によって動作特性が大きく変化し、実用に耐える物が得にくいという欠点もあった。耐熱性、耐水耐湿性、長波長での光透過性の優れる高分子材料を用いたもう一つの導波路作製の例としては、ベルフルオロ有機高分子材料を用いた光導波路（特開平4-190202号）がある。リッジ型導波路の1.3 μm 帯の導波路損失として0.1 dB/cm以下が実現されており、60℃温水中に1週間浸漬後も特性変化のないことが確認されている。しかしながら、これまでにベルフルオロ有機高分子材料の方向性結合器を含む導波路型デバイスへの適用例は無い。更に、ベルフルオロ有機高分子材料の熱光学効果は未検討であるため、熱光学効果を利用した適用例もない。

[0004]

【発明が解決しようとする課題】本発明の目的は、耐熱性、耐水耐湿性、光透過性に優れる高分子導波路型光デバイスを提供し、その結果として導波路型光デバイスの経済性、汎用性を改善することにある。

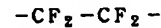
[0005]

【課題を解決するための手段】本発明を概説すれば、本発明は、分子鎖中に炭素-炭素一重結合と炭素-酸素一重結合からなる環状構造を有し、かつ炭素と一価元素の化学結合として炭素-フッ素結合のみを含む非晶質有機高分子材料であるベルフルオロ有機高分子材料を用いた導波路型光デバイスに関する発明であって、第1の発明の導波路型光デバイスは、コア及びクラッドのいずれか、又は両方がベルフルオロ有機高分子材料を主構成要素として形成された方向性結合器を含むことを特徴としている。第2の発明の導波路型光デバイスは、第1の発

明の方向性結合器を2個以上組合せて作製したマッハツェンダー干渉計を含むことを特徴とする。第3の発明の導波路型光デバイスは、第1の発明の導波路型光デバイスが、通電加熱を行うための抵抗体薄膜からなる熱光学位相シフタを有することを特徴とする。第4の発明の導波路型光デバイスは、第1~第3の発明の導波路型光デバイスにおけるベルフルオロ有機高分子材料が、下記構造式（化1）：

[0006]

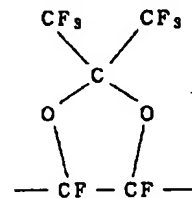
[化1]



[0007] 及び下記構造式（化2）：

[0008]

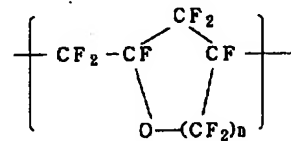
[化2]



[0009] からなる共重合体であることを特徴とする。更に、第5の発明の導波路型光デバイスは、第1~第3の発明の導波路型光デバイスにおけるベルフルオロ有機高分子材料が、下記構造式（化3）：

[0010]

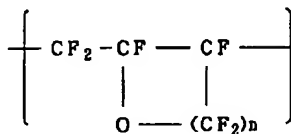
[化3]



[0011] 及び/又は下記構造式（化4）：

[0012]

[化4]



[0013]（ただし、nはいずれも1又は2）で表される繰り返し単位を有することを特徴とする。

[0014] 前記の観点から検討を進めた結果、本発明者らは、分子鎖中に炭素-炭素一重結合と炭素-酸素一重結合からなる環状構造を有し、かつ炭素と一価元素の化学結合として炭素-フッ素結合のみを含む非晶質有機高分子材料であるベルフルオロ有機高分子材料が、方向性結合器を含む導波路型光デバイス作製に必要な加工性を有することを明らかにした。その結果、作製したデバイスが波長1.3 μm 及び1.55 μm の近赤外域で低損失で、耐熱性、耐水耐湿性にも優れること、屈折率の

温度依存性を示す熱光学定数が他の高分子材料 ($10^{-4}/^{\circ}\text{C}$ 以上) と同等で石英よりも十分大きいこと、を見出し本発明を完成するに至った。

【0015】

【発明の実施の形態】以下、本発明を具体的に説明する。本発明に適用できるクラッド、コア材料について説明する。導波路型光デバイスが安定した性能を発揮するためには、前述したように、1) 導波路材料が近赤外域、特に波長 $1.3\mu\text{m}$ 及び $1.55\mu\text{m}$ 付近で透明であること、2) クラッド、コア材料が低吸湿・低吸水性、屈折率の環境湿度依存性が小さいこと、が望まれる。更に、熱光学効果を利用した導波路型光デバイスの場合には、クラッド、コア材料の熱光学定数と耐熱性もまた重要となる。

【0016】式(化1)で表される化合物と、式(化2)で表される化合物との共重合体(共重合比、35:65モル比)の吸収スペクトルをPMMAと比較して図1に示す。図1において、実線が当該共重合体、破線がPMMAのそれぞれ吸収スペクトルを示す。

【0017】図1に示すように、ベルフルオロ有機高分子材料は、従来のC-H結合を含む有機化合物では除くことができなかった波長 $1.1\mu\text{m}$ 、 $1.4\mu\text{m}$ 、 $1.65\mu\text{m}$ 付近のC-H結合の振動の倍音吸収を持たないため、 $0.6\sim 1.7\mu\text{m}$ の全域で高い透明性を有する。また、前述の共重合体や、式(化3)で $n=1$ の繰り返し構造を持つ化合物、式(化4)で $n=2$ の繰り返し構造を持つ化合物は、そのフィルム試料をASTM D570の方法で測定した吸水率が0.01%以下であることからわかるように、ベルフルオロ有機高分子材料は通常のPMMAの $1/100$ 以下、フッ素化ポリイミドに対しても $1/20$ 以下の小さな吸水率を有する。このため、ベルフルオロ有機高分子を用いて作製した方向性結合器は環境湿度によらず一定の特性を示し、環境湿度依存性が優れた導波路型光デバイスを作製できる。特に、従来の高分子材料では吸湿により波長 $1.4\mu\text{m}$ のO-H結合の振動の倍音吸収が増加して、 $1.3\mu\text{m}$ 及び $1.55\mu\text{m}$ の光損失増加が観測されたのに対して、本発明のベルフルオロ有機高分子を用いた導波路型光デバイスでは、高湿度条件においても損失変動は小さな値であった。更に、ベルフルオロ有機高分子材料で作製したマッハツェンダー型熱光学効果スイッチは、スイッチング電力が石英系光導波路に比べて $1/100$ 程度となり、PMMAの場合と同程度の大きな熱光学効果を有していた。また、スイッチング特性の湿度依存性も観測されず、安定した特性を実現できた。

【0018】本発明に用いるベルフルオロ有機高分子材料としては、分子内にC-H結合を持たず、炭素と一価元素の化学結合として炭素-フッ素結合のみを含む非晶質プラスチックであれば、どのようなものでも使用することができる。中でも、プラスチックの分子構造にお

る対称性を無くし非晶性を高めることによって配向複屈折に伴う光の散乱を抑える観点から、高分子の主鎖構造中に環状エーテル構造、つまり炭素-炭素一重結合と炭素-酸素一重結合からなる環状構造を有するプラスチックが好適に使用できる。

【0019】以下、本発明の光導波路デバイスについてより詳細に説明する。本発明の光導波路デバイスのうち、方向性結合器、及びマッハツェンダー干渉計の一般的な作製工程を図2に示す。最初に、基板1上に下部クラッド層2を形成する。次に、下部クラッド層2上へ、下部クラッド層2よりも屈折率の大きなコア層3を形成する。次に、コア層3上へフォトリソグラフ法によって方向性結合器又はマッハツェンダー干渉計のマスクパターン4を形成する。マスクパターン4が形成されたコア層3に対して、RIE法を用いてエッチングを行い方向性結合器のコアパターン5を形成する。マスクを除去した後、方向性結合器のコアパターン5上に上部クラッド層6を形成する。このような方法によって、ベルフルオロ有機高分子光導波路による方向性結合器(図3)、及びマッハツェンダー干渉計(図4)が形成される。すなわち、図3及び図4は、それぞれの模式図である。

【0020】方向性結合器は導波路型光デバイスを構成する要素の中で、最も重要、かつ基本的なものの一つである。単体では出射光を任意の比率で分岐させる光部品として用いられ、その分岐比は相互作用長を変えることにより制御できる。また、マッハツェンダー干渉計は導波路型光デバイスを構成する基本光回路であり、位相シフタとの組合せにより種々の光部品として利用できる。本発明においては、導波路材料として用いたベルフルオロ有機高分子材料の耐熱性、耐水耐湿性、光損失特性が優れることを利用して高温条件や高温高湿条件で長時間使用しても特性変化の小さい方向性結合器及びマッハツェンダー干渉計を容易に作製できるようになり、方向性結合器及びマッハツェンダー干渉計を有する導波路型光デバイスの耐環境性、経済性、汎用性が大幅に向上した。

【0021】図5は、ベルフルオロ有機高分子光導波路を用いて形成したマッハツェンダー干渉計と、抵抗体薄膜による加熱用電極からなるT0スイッチの作製工程を示す図である。図2と同様の方法で作製したマッハツェンダー干渉計の上部クラッド層6上に金属膜7を形成する。次にこの金属膜7上へフォトリソグラフ法により加熱用電極(熱光学位相シフタ)のマスクパターン8を形成した後、金属膜7のエッチングを行い加熱用電極9を形成する。このような方法によって、ベルフルオロ有機高分子光導波路によるマッハツェンダー型T0スイッチ(図6、模式図)が形成される。本発明においては、光導波路材料に耐熱性、耐水耐湿性の優れたベルフルオロ有機高分子を用いているため、耐環境性、長期安定性に優れ、石英系T0スイッチよりも低電力、かつ高速でス

エッチングするペルフルオロ有機高分子T Oスイッチが容易に形成できるようになった。また、他の高分子材料で作製したT Oスイッチに比べて、湿気や水分の侵入を防止する封止等の措置を施さない状態でも広い湿度条件下ではば一定の動作特性を示すこともわかった。その結果、高分子T Oスイッチの耐環境性、経済性、汎用性を大幅に向上させることができた。なお、本発明では、任意の基板材料を用いることができるが、熱伝導率の大きなAl、Al合金、ステンレス、銅、等の基板材料を用いた方がスイッチング速度は早くなる。また、抵抗体薄膜形成用の材料としては、Ti、Cr、Al、金、銀、銅、白金、酸化スズ、酸化インジウム、酸化インジウムスズ、及びこれらの混合物が使用できる。またこれらの薄膜の積層膜であっても良い。

【0022】なお、上記に示した導波路型光デバイスの作製工程においては、クラッド材料の上にコア材料をスピンコートするとき、及びコア材料の上にクラッド材料をスピンコートするとき等に、先に塗布してあった材料が溶解して後から塗布する材料と混じり合うインターミキシングが発生する可能性がある。本発明では、コアやクラッドと共通溶媒を持たない材料を使用して薄膜のインターミキシング防止層を設けても良いことはいうまでもない。この防止層の材料は、無機材料、有機材料のどちらでもよく、無機材料としてはSiO₂、やMgF₂、CaF₂、等が、また有機材料としてはペルフルオロ有機高分子のほかポリイミド、シリコン高分子等が使用できる。作製方法は、抵抗加熱、電子ビーム加熱、スパッタリング等の各種真空蒸着法のほか、スピンオンガラス法、スピンコート法が利用可能である。

【0023】

【実施例】以下、図面を用いて本発明を更に具体的に説明するが、本発明はこれら実施例に限定されない。なお本実施例では、基板にセラミックやシリコン、金属膜にTi、金を用いているが、他の材料を用いても良いことはいうまでもない。

【0024】実施例1

式(化1)の構造であるテトラフルオロエチレンと、式(化2)の構造であるビス-2, 2-トリフルオロメチル-4, 5-ジフルオロ-1, 3-ジオキソール(PPD)との共重合体のうち、PPDの共重合比が83mol%の高分子をフッ素系の有機溶媒(Fluorinert FC-75, 3M社製)に濃度が2%となるように溶解した。溶液をセラミック基板上にスピンコートして、窒素雰囲気下40℃で1時間、100℃で1時間、180℃で1時間加熱し、溶媒を完全に除去して、膜厚15μm、波長0.59μmでの屈折率が1.29の下部クラッド層2を作製した。次に、PPDの共重合比が40mol%の高分子をフッ素系の有機溶媒(Fluorinert FC-75, 3M社製)に濃度が10%となるように溶解し、溶液をセラミック基板上にスピンコートして、窒素

雰囲気下40℃で1時間、100℃で1時間、180℃で1時間加熱し、溶媒を完全に除去して、膜厚7μm、波長0.59μmでの屈折率が1.32のコア層3を作製した。この試料全面にエッチング用マスクとしてチタンを電子線加熱法で蒸着した。次いでポジ型レジストの塗布、プリベーク、露光、現像、ポストベークを行い、チタンをウェットエッチングによりパターニングして方向性結合器のマスクパターン4を作製した。更にこのチタンをマスクとして、ビス-2, 2-トリフルオロメチル-4, 5-ジフルオロ-1, 3-ジオキソール(PPD)と、テトラフルオロエチレンとの共重合体のフィルムをドライエッチングによりパターニングし、コアパターン5を作製した。残ったチタンをウェットエッチングにより除去し、最後に下部クラッドを作製したのと同様の方法で厚さ5μmの上部クラッド6を作製した。このような方法により、コア幅7μm、コア高さ7μmの埋込型導波路で形成した図3の構造の方向性結合器を得た。コアとクラッドの間の屈折率差Δは波長1.3μmで約0.25%であった。この方向性結合器は、相互作用長を適当に選ぶことにより、波長1.3μmの時、TE偏光及びTM偏光共に結合率97%以上、接続損失を含む挿入損失2dB、3dBカップラーの過剰損失0.2dBと優れた光学特性を示した。更に、波長1.2μm~1.65μmの全波長域において、TE偏光及びTM偏光共に結合率95%以上、接続損失を含む挿入損失2.3dB、3dBのカップラーの過剰損失0.3dB以下の方向性結合器を得た。作製した方向性結合器は100℃熱処理後、及び水中、高温高湿(85℃、85%RH)雰囲気中やアセトン中に浸漬後も初期と同等の特性を有しており、耐環境性、長期安定性に優れたものであった。この結果、式(化1)と式(化2)の共重合体のペルフルオロ高分子を使用することにより、方向性結合器を有する導波路型光デバイスの耐環境性、経済性、汎用性は大幅に向上した。

【0025】実施例2

実施例1においてコア層3として用いたペルフルオロ高分子[ビス-2, 2-トリフルオロメチル-4, 5-ジフルオロ-1, 3-ジオキソール(PPD)とテトラフルオロエチレンとの共重合体]の代りに、式(化3)でn=1の繰返し構造を持つポリペルフルオロアリルビニルエーテル(波長0.59μmでの薄膜の屈折率は1.34)を、またコア層作製のスピンコート溶媒としてフッ素系の有機溶媒(Fluorinert FC-75, 3M社製)の代りにペルフルオロ有機溶媒(CT-solv 180, 旭硝子社製)を、基板としてセラミック板の代りにSiウエハーを使用して実施例1と同様にコア幅7μm、コア高さ7μmの埋込型導波路で形成した図3の構造の方向性結合器を得た。コアとクラッドの間の屈折率差Δは波長1.3μmで約0.35%であった。この方向性結合器は、波長1.3μmの時、TE偏光及びT

M偏光共に結合率97%以上、接続損失を含む挿入損失2dB、3dBカップラーの過剰損失0.2dBと優れた光学特性を示した。更に、波長1.2 μ m~1.65 μ mの全波長域において、TE偏光及びTM偏光共に結合率95%以上、接続損失を含む挿入損失2.3dB以下、3dBのカップラーの過剰損失0.3dB以下の方向性結合器を得た。作製した方向性結合器は100℃熱処理後、及び水中、高温高湿(85℃、85%RH)雰囲気中やアセトン中に浸漬後も初期と同等の特性を有しており、耐環境性、長期安定性に優れたものであった。この結果、式(化3)でn=1の繰り返し構造を持つポリベフルオロアリルビニルエーテルを使用することにより、方向性結合器を有する導波路型光デバイスの耐環境性、経済性、汎用性は大幅に向上した。

【0026】実施例3

実施例1のマスクパターン4を、3dBカップラーを2個連結した構造のマッハツェンダー干渉計に変更し、実施例1と同様の操作を行うことにより、コア幅7 μ m、コア高さ7 μ mの埋込型導波路で形成した図4の構造のマッハツェンダー干渉計を得た。このマッハツェンダー干渉計に波長1.3 μ mの光をアーム1から入力したところ、光出力はアーム4でのみ観測された。このときの挿入損失は結合損失込みで2.5dBと小さな値を示した。作製したマッハツェンダー干渉計は100℃熱処理後、及び水中、高温高湿(85℃、85%RH)雰囲気中やアセトン中に浸漬後も初期と同等の特性を有しており、耐環境性、長期安定性に優れたものであった。また、環境湿度が13~90%RHの範囲でほぼ同等の特性を示し、従来の高分子導波路で問題であった分岐比の動作湿度依存性も解消された。更に、波長1.2 μ m~1.65 μ mで3dBカップラーを使用することにより全波長域において1.3 μ mの場合と同様の結果を得ることが可能であった。この結果、式(化1)と式(化2)との共重合体のベフルオロ高分子を使用することにより、マッハツェンダー干渉計を有する導波路型光デバイスの耐環境性、経済性、汎用性は大幅に向上した。

【0027】実施例4

実施例2のマスクパターン4を、3dBカップラーを2個連結した構造のマッハツェンダー干渉計に変更し、実施例2と同様の操作を行うことにより、コア幅7 μ m、コア高さ7 μ mの埋込型導波路で形成した図4の構造のマッハツェンダー干渉計を得た。このマッハツェンダー干渉計に波長1.3 μ mの光をアーム1から入力したところ、光出力はアーム4でのみ観測された。このときの挿入損失は結合損失込みで2.6dBと小さな値を示した。作製したマッハツェンダー干渉計は100℃熱処理後、及び水中、高温高湿(85℃、85%RH)雰囲気中やアセトン中に浸漬後も初期と同等の特性を有しており、耐環境性、長期安定性に優れたものであった。また、環境湿度が13~90%RHの範囲でほぼ同等の特

性を示し、従来の高分子導波路で問題であった分岐比の動作湿度依存性も解消された。更に、波長1.2 μ m~1.65 μ mで3dBカップラーを使用することにより全波長域において1.3 μ mの場合と同様の結果を得ることが可能であった。この結果、式(化3)でn=1の繰り返し構造を持つポリベフルオロアリルビニルエーテルを使用することにより、マッハツェンダー干渉計を有する導波路型光デバイスの耐環境性、経済性、汎用性は大幅に向上した。

【0028】実施例5

実施例3で作製したマッハツェンダー干渉計の上部クラッド層6の上に加熱用電極(熱光学位相シフタ)とするTi金属膜7をスパッタ蒸着により形成した。このTi金属膜7へフォトリソグراف法をスピンコートした後、電極のマスクパターン8をフォトリソグراف法によってレジストに転写させた。最後に、フォトリソグراف法をマスクとし、Tiのエッチングを行い電極9を形成した。このような方法によって形成したベフルオロ有機高分子光導波路によるマッハツェンダー型TOSスイッチ(図6)の特性測定を行った結果、スイッチング時間は4mS、スイッチング電力は8mWで、このときの透過ポートの挿入損失は接続損失込みで2.5dB、スイッチングの消光比は25dBであった。式(化1)と式(化2)との共重合体のベフルオロ高分子が有する大きな熱光学定数の効果によりスイッチング電力は石英製の1/50以下であり、作製したベフルオロ有機高分子TOSスイッチが低電力、高速光スイッチとして動作することがわかった。また、作製したTOSスイッチは100℃熱処理後、及び水中、高温高湿(85℃、85%RH)雰囲気中やアセトン中に浸漬後も初期と同等の特性を有しており、耐環境性、長期安定性に優れたものであった。更に、環境湿度が13~90%RHの範囲でほぼ同等の特性を示し、従来の高分子導波路で問題であったスイッチングの消光比の動作湿度依存性も解消された。この結果、式(化1)と式(化2)との共重合体のベフルオロ高分子を使用することにより、高分子TOSスイッチの耐環境性、経済性、汎用性を大幅に向上させることができた。

【0029】実施例6

実施例4で作製したマッハツェンダー干渉計の上部クラッド層6の上に加熱用電極(熱光学位相シフタ)とするTiと金の2層金属膜7をスパッタ蒸着により形成した。この金属膜7へフォトリソグراف法をスピンコートした後、電極のマスクパターン8をフォトリソグراف法によってレジストに転写させた。最後に、フォトリソグراف法をマスクとし、Tiのエッチングを行い電極9を形成した。このような方法によって形成したポリベフルオロアリルビニルエーテル光導波路によるマッハツェンダー型TOSスイッチ(図6)の特性測定を行った結果、スイッチング時間は5mS、スイッチング電力は7mWで、

このときの透過ポートの挿入損失は接続損失込みで2.6 dB、スイッチングの消光比は25 dBであった。式(化3)で $n=1$ の繰返し構造を持つポリベルフルオロアリルビニルエーテルが有する大きな熱光学定数の効果によりスイッチング電力は石英製の1/50以下であり、作製したベルフルオロ有機高分子TOSスイッチが低電力、高速光スイッチとして動作することがわかった。また、作製したTOSスイッチは100℃熱処理後、及び水中、高温高湿(85℃、85%RH)雰囲気中やアセトン中に浸漬後も初期と同等の特性を有しており、耐環境性、長期安定性に優れたものであった。更に、環境湿度が13~90%RHの範囲でほぼ同等の特性を示し、従来の高分子導波路で問題であったスイッチングの消光比の動作湿度依存性も解消された。この結果、式(化3)で $n=1$ の繰返し構造を持つポリベルフルオロアリルビニルエーテルを使用することにより、高分子TOSスイッチの耐環境性、経済性、汎用性を大幅に向上させることができた。

【0030】実施例7

実施例6で使用した、式(化3)で $n=1$ の繰返し構造を持つポリベルフルオロアリルビニルエーテルの代りに、式(化3)で $n=2$ の繰返し構造を持つポリベルフルオロアリルビニルエーテル、式(化4)で $n=1$ の繰返し構造を持つポリベルフルオロアリルビニルエーテル、及び式(化4)で $n=2$ の繰返し構造を持つポリベルフルオロアリルビニルエーテルを用いて実施例6と同様の操作を行い、ポリベルフルオロアリルビニルエーテル光導波路によるマッハツェンダー型TOSスイッチを作製した。その特性測定を行った結果、スイッチング時間、スイッチング電力、透過ポートの挿入損失、スイッチングの消光比共に実施例6で作製したスイッチの±10%の範囲でほぼ同等の値を示した。また、100℃熱処理後、及び水中、高温高湿(85℃、85%RH)雰囲気中やアセトン中に浸漬後も初期と同等の特性を有しており、耐環境性、長期安定性に優れたものであった。更に、環境湿度が13~90%RHの範囲でほぼ同等の特性を示し、従来の高分子導波路で問題であったスイッチングの消光比の動作湿度依存性も解消された。この結果、式(化3)で $n=2$ の繰返し構造を持つポリベルフルオロアリルビニルエーテルや、式(化4)で $n=1$ の繰返し構造を持つポリベルフルオロアリルビニルエーテル、及び式(化4)で $n=2$ の繰返し構造を持つポリベルフルオロアリルビニルエーテルを使用することによっても、高分子TOSスイッチの耐環境性、経済性、汎用性を大幅に向上させることができた。

【0031】比較例1

コア材料としてPMMA、クラッド材料として部分フッ素化PMMAを使用し、実施例3と同様な方法でマッハツェンダー干渉計を作製した。このマッハツェンダー干渉計に波長1.3μmの光をアーム1から入力したと

ろ、環境湿度50%の時に光出力はアーム4でのみ観測された。このときの挿入損失は結合損失込みで2.3 dBと小さな値を示した。しかし、CH結合の倍音吸収ピークがある1.1、1.4、1.6μm帯では10 dB以上の大きな挿入損失を示した。作製したマッハツェンダー干渉計は100℃熱処理後、及び水中、高温高湿(85℃、85%RH)雰囲気中やアセトン中に浸漬後は挿入損失が5 dB以上に増加し、耐環境性、長期安定性が劣っていることがわかった。また、環境湿度が13~90%RHの範囲でアーム4の出力が徐々に減少しアーム3の出力が増加した。この結果、PMMAをコア材料とするマッハツェンダー干渉計では耐環境性、経済性、汎用性が劣っている。

【0032】比較例2

コア材料としてPMMA、クラッド材料として部分フッ素化PMMAを使用し、実施例5と同様な方法でマッハツェンダー干渉計型TOSスイッチを作製した。このマッハツェンダー型TOSスイッチ(図6)の特性測定を行った結果、スイッチング時間は5 mS、スイッチング電力は8 mWで、このときの透過ポートの挿入損失は接続損失込みで2.5 dB、スイッチングの消光比は25 dBであった。作製したTOSスイッチを100℃熱処理後、及び水中、高温高湿(85℃、85%RH)雰囲気中やアセトン中に浸漬後に特性を測定したところ、挿入損失が5 dB以上に増加し、耐環境性、長期安定性が劣っていた。また、環境湿度を13~90%RHの範囲で変化させたところ、同一の動作条件でスイッチングの消光比が最悪で5 dBまで低下し、光スイッチとして不十分な動作特性となる。この結果、PMMAをコア材料とするマッハツェンダー干渉計型TOSスイッチでは耐環境性、経済性、汎用性が劣っている。

【0033】

【発明の効果】本発明によれば、導波路材料として使用したベルフルオロ有機高分子の耐熱性、耐水耐湿性、高光透過性の特徴により、耐熱性、耐水耐湿性、光損失特性に優れた高分子導波路型光デバイスを提供できる。また、その結果として経済性、汎用性に優れた導波路型光デバイスが製造できるようになった。

【図面の簡単な説明】

【図1】ベルフルオロ高分子とPMMAの吸収スペクトルを示す図である。

【図2】方向性結合器及びマッハツェンダー干渉計の作製工程を示す図である。

【図3】方向性結合器の模式図である。

【図4】マッハツェンダー干渉計の模式図である。

【図5】フッ素化ポリイミドによるTOSスイッチの作製工程を示す図である。

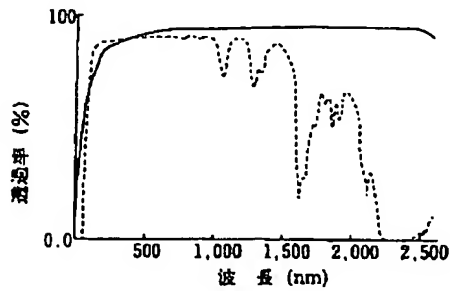
【図6】フッ素化ポリイミドTOSスイッチの模式図である。

【符号の説明】

1:基板、2:下部クラッド層、3:コア層、4:マスクパターン、5:コアパターン、6:上部クラッド層、*

* 7:金属膜、8:電極のマスクパターン、9:電極

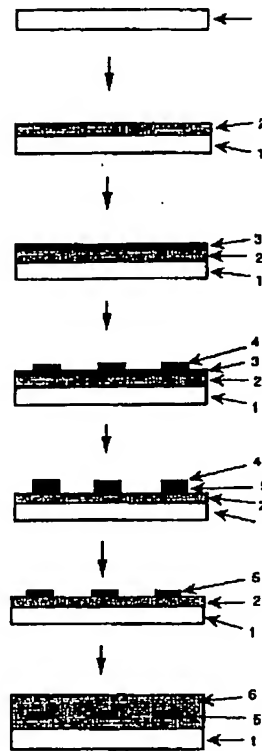
【図1】



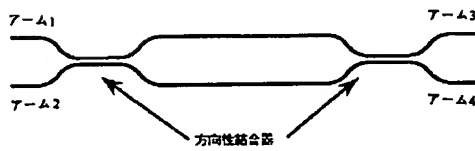
【図3】



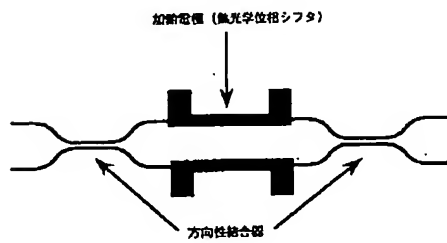
【図2】



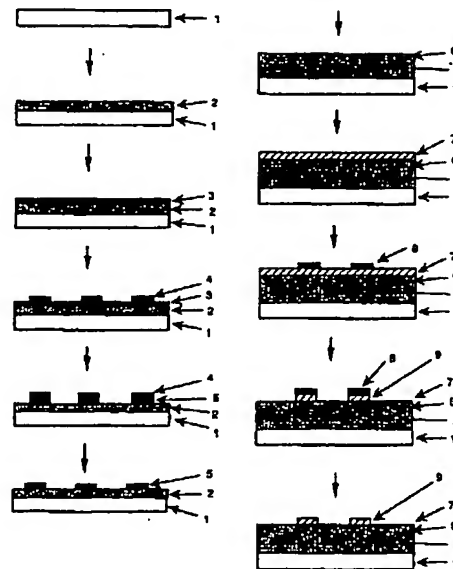
【図4】



【図6】



【図5】



フロントページの続き

(72)発明者 松浦 徹
東京都新宿区西新宿三丁目19番2号 日本
電信電話株式会社内

(72)発明者 佐々木 重邦
東京都新宿区西新宿三丁目19番2号 日本
電信電話株式会社内